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TECHNICAL REPORT 55-26

PART III

RESEARCH ON BORON POLYMERS

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RUTGERS UNIVERSITY

MAY 1956

WRIGHT AIR DEVELOPMENT CENTER

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RESEARCH ON BORON POLYMERS

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AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared at the School of Chemistry, Rutgers University, New Brunswick, New Jersey under USAF Contract No. AF33(616)2057. This contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials", Task No. 73404, "Synthesis and Evaluation of New Polymers" formerly RDO No. 617-11, "Synthesis and Evaluation of New Polymers", and was administered by the Organic Materials Branch, Materials Laboratory, with Major William Postelnek, Lt. Malcolm J. Rogers, Jr., and Lt. Douglas A. Rausch acting as project engineers.

This report covers period of work from December, 1954 to December 1955.

The personnel assigned to this project were Dr. William L. Ruigh, Principal Investigator, with two part-time research assistants, Mr. Frank C. Gunderloy and Mr. Michael Sedlak. A third part-time research assistant, Mr. Nathan Steinberg was added to the group as of September 15, 1955. Staff consultants on this project were Drs. Charles E. Erickson and P. A. van der Meulen. A secretary, part-time, was also assigned.

ABSTRACT

A new, simple, and efficient synthesis of boron substituted borazoles has been developed. Butylboron dichloride reacts with ammonia to give a high yield of B-tributylborazole. This synthesis will be broadened by the employment of substituted amines. Some of the resulting B-N substituted borazoles may serve as the basis of thermally and hydrolytically stable semi-inorganic polymers and the liquid borazoles will be evaluated as lubricants and hydraulic fluids.
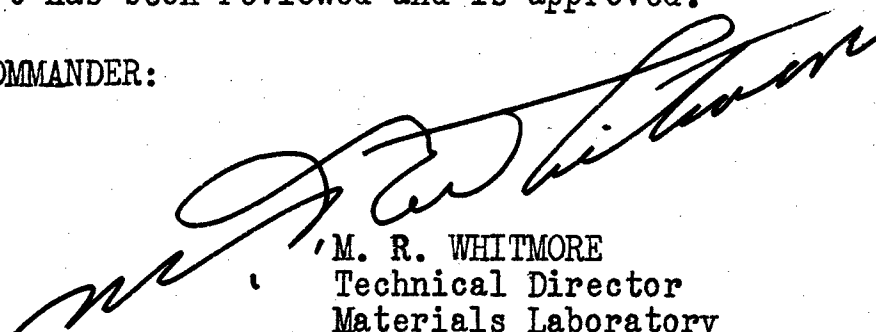
The preparation of benzeneboronic acid, tri-n-butylborine, butylboron dichloride and phenylboron dichloride as intermediates for our new borazole synthesis has been studied.

A new catalytic recirculating apparatus for preparing phenylboron dichloride from benzene and boron trichloride by Pace's method is described.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
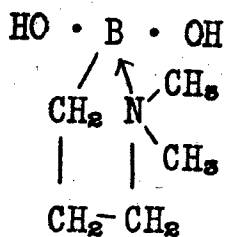Materials Laboratory
Directorate of Research

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I. UNDERLINE INTRODUCTION

This report covers a project on "Research on Boron Polymers" for the twelve-month period 1 December 1954 to 30 November 1955. This work is a part of an Air Force continuous study program, the broad objective of which is to prepare and investigate new hydrolytically stable polymeric materials possessing exceptional fuel and oil resistance, high thermal stability and other properties of critical importance for specialized Air Force Applications. Another purpose of this work, which has developed particularily in the past year, is the preparation of certain materials for evaluation as hydraulic fluids and lubricants.

Since the inception of this work at Rutgers in June 1953, nine bimonthly reports, A-1 to A-9, have been issued and are now out of print. An Air Force Technical Report in two parts covering this work is at present in the process of reproduction. WADC Technical Report 55-26, Part 1 consists of a literature survey in the field of boron polymers together with pertinent references in the general field of inorganic and semi-inorganic polymers (1). The second part of this report (WADC Technical Report 55-26, Part 2) describes the experimental work on the project carried out over the eighteen month period, 1 June 1953 to 30 November 1954 (2).

The present report is concerned primarily with two problems: (a) the attempted synthesis of a "scorpion" boronic acid, γ-dimethylaminopropaneboronic acid, (formula I), and (b) the preparation of a boron substituted alkylborazoles (formula II) by a new, simple, and efficient synthesis. Both problems have for their main objective the preparation of monomers for the synthesis of boron polymers. The borazoles in addition will be evaluated as thermally stable, hydraulic fluids and lubricants.

$$HO \cdot B \cdot OH$$

```
        HO · B · OH
          /  ↖ \CH₃
       CH₂  N
         |   | \CH₃
         |   |
       CH₂─CH₂
```

```
              R
              |
              B
            /   \
        HN      NH
         |       |
       R-B      B-R
            \   /
              N
              |
              H
```

I	II
γ-Dimethylaminopropaneboronic Acid ("Scorpion" type boronic acid)	B-alkyl or aryl borazole
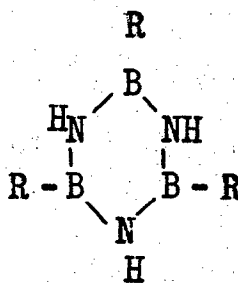
II. LITERATURE SURVEY AND DISCUSSION

Booth and Kraus (3) reported a very stable polymeric boron-nitrogen compound which they described as "n-butyl-boronimine" resulting from the reaction of n-butylboron dichloride and ammonia in the presence of sodium. This subject has been discussed in earlier reports (2).

Another polymer described in the same paper was a polymeric di-n-butylboronamine formed from the reaction of di-n-butylboron chloride with ammonia in the presence of sodium. This polymer appeared to react readily with hydrogen peroxide and dilute hydrochloric acid with immediate formation of a homogeneous solution.

The "n-butylboronimine" polymer (from n-butylboron dichloride) was resistant to hydrolysis even when treated with a dilute solution of sodium hydroxide and hydrogen peroxide. Finally, the material was dissolved in concentrated sulfuric acid and decomposed by heating and the later addition of 30 percent hydrogen peroxide. Boron and nitrogen analyses on the resulting solution were in good agreement with the calculated n-butylboronimine formula. Booth and Kraus did not discuss the structural formula of the polymer but an obvious structure is shown in formula III.

$$\left[\begin{array}{cccc} - B & - N & - B & - N - \\ | & | & | & | \\ Bu & H & Bu & H \end{array} \right]_x$$

III
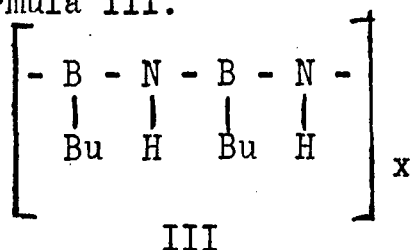
n-butylboronimine
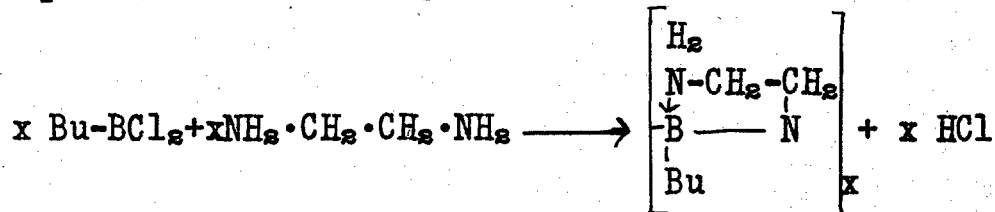
Whether the material had linear or cyclic structure or a mixture of both forms as in the case of the silicones can not be deduced from the data given in the original paper.

At the WADC Contractors' Meeting in September 1954, we proposed to proceed with the repetition of the work of Booth and Kraus and to extend the reaction to include diamines of three general classes i.e., aliphatic

(ethylenediamine) aromatic (phenylenediamine) and
heterocyclic (2-aminomethylpyridine). (The use of 2-
aminomethylpyridine was suggested by Dr. C. S. Marvel
and, if steric factors do not interfere, would lead to
a polymer of enhanced thermal stability). The objective
in using diamines was to extend the idea embodied in the
"scorpion" boronic acids to form "scorpion" polymers
with quadricovalent nitrogen as illustrated below (IV).

$$x \ Bu\text{-}BCl_2 + xNH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2 \longrightarrow \left[\begin{array}{c} H_2 \\ N\text{-}CH_2\text{-}CH_2 \\ \downarrow \qquad \qquad | \\ B \text{------} N \\ | \\ Bu \end{array} \right]_x + x \ HCl$$

IV

Incidental to the repetition of Booth and Kraus'
work we prepared a quantity of the intermediate n-
butylboron dichloride by a new synthesis described in
our previous report (2).

n-Butylboron dichloride was reacted with ammonia
in the presence of sodium, the product worked up by a
modified extraction procedure and distilled in a high
vacuum still. The main product, instead of distilling
at 100-110° C at a pressure of 5 microns, as reported
by Booth and Kraus, came over at 34° at 7 microns. It
was immediately suspected that the product was tri-B-
n-butylborazole (Mol. wt. 248.84). A $C_{18}H_{30}$ aromatic
hydrocarbon, tri-tert-butylbenzene (Mol. wt. 246.42) was
reported to boil at 296-305° C at 760 mm. Extrapolation
of this value by a vapor-pressure-temperature nomograph
combined with a further graphical extrapolation of log
p vs 1/T gave a value for the boiling point of 33° C
at 10 microns and 24° C at 5 microns.

The process of extrapolation was applied to the
higher boiling point (105° C at 5 microns) reported by
Booth and Kraus. In this case the material would appear
to have a molecular weight slightly less than the hexamer
($C_{24}H_{60}N_6B_6$). It would appear possible that the boiling
point-vapor pressure relationship recorded by Booth and
Kraus was subject to experimental error and that, in fact,
the material they had was butylborazole. The absolute
pressure at the surface of the evaporating liquid was

possibly considerably higher than 5 microns.

The material obtained from our reaction was further investigated and found to be B-n-butylborazole as shown by analytical data,molecular weight determinations and particularly the infrared spectrum. An analysis of its spectrum in comparison to borazole itself is given in the experimental section.

It was noted in the first run that the butylboron dichloride appeared to react with the ammonia before the addition of sodium. In a second run the sodium was omitted and the yield of B-n-butylborazole was doubled. The yield of distilled product in the sodium run was 29.6% and in the second run 63.2% (with a crude yield of 74.6%). The small scale of these runs and the relatively crude methods of handling the borazole, both in working up the reaction and in distillation, made it probable that the yield could be very considerably improved. Quantitative yields of borazole from this reaction would appear to be a possibility in large scale operations.

Our current work on tri-B-phenylborazole appears to give yields of 90 percent or better (99% + when the crude mother liquor fraction is included) when the reaction is modified by diluting the phenylboron dichloride with a solvent such as benzene and introducing a slow stream of gaseous ammonia. The product of this reaction is a white crystalline solid, m.p. 184°, which appears to be tri-B-phenylborazole from infrared and molecular weight determinations. The analyses are somewhat low and as yet unsatisfactory and the problem is still being investigated.

On June 1, 1955, a conference was held at the Materials Laboratory, WADC. It was decided to suspend for the time being that part of the work dealing with the synthesis of γ-dimethylaminopropaneboronic acid and similar "scorpion" acids containing quadricovalent boron. This decision was reached largely on the basis of the greater promise of practical utility of the substituted borazoles. In addition to the semi-inorganic polymer program based on our new borazole synthesis there appeared to be considerable interest in the possible application of these new boron-substituted borazoles in the field of high temperature lubricants and hydraulic fluids.

Tri-n-butyl-B-borazole was found to be unexpectedly
more hydrolytically stable than the literature predicts
for relatively unhindered B-substituted borazoles. This
fact coupled with the reported very high thermal stability
(500° C or 932° F) of substituted borazoles such as hexa-
methylborazole (4) makes an evaluation of these materials
of immediate interest.

Due to the existing standards for testing lubricants
and hydraulic fluids the size of sample required for pre-
liminary work was fixed at 50-100 ml. Most published
work on borazoles has been done in a "vacuum chain" with
quantities of milliliters of gas and in much less than
gram quantities. Although our new borazole synthesis is
more adaptable to scaling up the size of run than prior
methods, nevertheless, a reinvestigation of the methods
for preparing our intermediate alkyl and aryl boron di-
chlorides is essential to the preparation of the borazoles
in adequate amounts for testing.

Earlier in this section we described a new general
synthesis of boron substituted borazoles which could also
be used for mixed boron and nitrogen substituted borazoles.

$$3 \, R \cdot BCl_2 + 3 \, R'NH_2 \longrightarrow R_3R_3'N_3B_3 + 6HCl$$
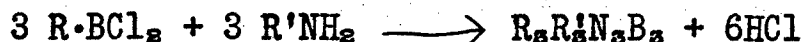
The specific example of this synthesis given was the
preparation of tri-n-butyl-B-borazole from n-butylboron
dichloride and ammonia. The quantities of borazole ob-
tained in two exploratory runs was of the order of 1 to
2 grams. The largest amount of a borazole obtained pre-
viously was produced recently by the cooperative research
of the University of Chicago with the Naval Research
Laboratory (5). The product of "several" runs of borazole
obtained by the reduction of trichloroborazole with
lithium aluminum hydride was thirteen grams (5). Our
new synthesis is more readily capable of scaling up than
any previously described method.

Primarily because of the size of samples required
for the evaluation as lubricants and hydraulic fluids the
work was thus directed toward the preparation of the
intermediates, butylboron dichloride and phenylboron
dichloride and starting materials such as tri-n-butyl-
borine and benzeneboronic acid.

Very little has been published on the synthesis of the intermediate alkyl and arylboron dihalides. While this work was in progress a paper was given at the September 1955 A.C.S. Meeting by P. A. McCusker et. al. on the "Preparation and Properties of Some Organodichloroboranes".

For our work we required butylboron dichloride and phenylboron dichloride. The preparation of the former was first described by Booth and Kraus (3) by a two-step process involving the isolation of pure dibutylboron monochloride.

$$\text{I} \quad Bu_3B + HCl \xrightarrow[110°C]{} Bu_2BCl + C_4H_{10}$$

$$\text{II} \quad 2Bu_2BCl + HCl \xrightarrow[110°]{AlCl_3} BuBCl_2 + BCl_3 + C_4H_{10}$$
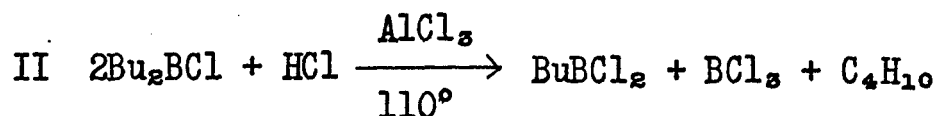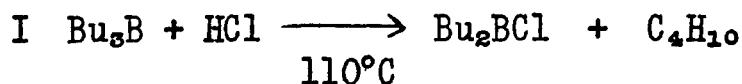
The equations are not balanced. Booth and Kraus reported equal quantities of the dichloride and boron trichloride formed in step two. In addition to butane, some butylene is formed. When butylborine was treated with HCl at 180-210° the same products as in equation II were obtained but in addition the presence of the monochloride made the mixture difficult to separate by distillation. (The boiling points areas follow: $Bu_3B = 211°$ C; $Bu_2BCl = 173°$ C; $BuBl_2 = 108°$ C; $BCl_3 = 12°$ C). The preparation of the monochloride was repeated by Skinner and Tees (6). The meager literature on the alkylhalogen borines has been reviewed recently by Long and Dollimore (7,8) who mention the conflicting reports on their disproportionation and also confirm our own and Skinner and Tees' (6) observation that the chloroborines are spontaneously inflammable, igniting more readily even than the borines.

In an earlier report (2) we described the preparation of n-butylboron dichloride by a new synthesis in which the borine is heated to 110° with boron trichloride in the presence of $AlCl_3$ and an excess of refluxing boron

trichloride.

$$Bu_3B + 2 BCl_3 \xrightarrow[110°]{AlCl_3} 3 BuBCl_2$$
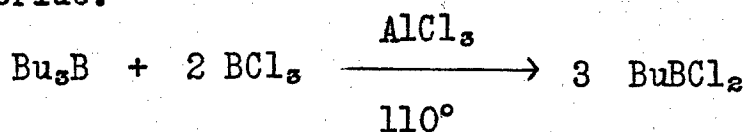
The yield of crude butylboron dichloride was reported as 35.4% based on the tributylborine but the final yield of pure product only 10%. The drop in yield was ascribed to excessive losses in fractionating the product. Another cause of the poor yield was thought to be the possible presence of oxidation products in the borine used. During this period the work was repeated on a fresh, analytically pure sample of n-butylborine with added precautions and refinements in our technique of handling and fractionation. In the new run the yield was 8% or even less than the 10 percent previously obtained. We could speculate on the cause of the low yield in this disproportionation reaction but prefer to await further facts. At present the yields in the two-step Booth and Kraus process are being determined. In spite of the loss of butyl groups as butane, it may well be that the original process is preferable to our own which appears superior on paper due to the conservation of all butyl groups.

Phenylboron dichloride was chosen as the intermediate for the synthesis of triaryl boron substituted borazoles.

$$3 C_6H_5BCl_2 + 3 NH_2R \longrightarrow [(C_6H_5)B]_3[R \cdot N]_3 + 6 HCl$$

The arylboron dihalides have been prepared previously by the action of boron trihalide on mercury or zinc diphenyl. Thus, Michaelis and his coworkers prepared phenylboron dichloride from the reaction of BCl_3 on mercury diphenyl (11) and used the same reaction for alkyl benzene derivatives (12). Phenylboron difluoride was prepared from BF_3 and diphenyl zinc (13). The subject of phenylboron dihalides and esters has recently been reviewed by Torssell (14).

It is curious that an obvious route to the dihalides via the halogenation of the boronic acids has been so

little explored. We made an attempt in 1953 to prepare phenylboron dichloride by the reaction of phosphorus pentachloride on benzeneboronic acid but were unsuccessful. With the exception of the early work of Burg with BF_3 (9) and the more recent work of McCusker (10) no other published work is available.

Prior to our decision to prepare phenylboron dichloride by a catalytic route from benzene and BCl_3 we expected to synthesize this intermediate from benzeneboronic acid. In our previous report (2) we described improvements in the Grignard synthesis from methyl borate and phenyl magnesium halide. Since then we have continued to improve the process until a yield of 70 percent or better was consistently obtained. The recent literature reports yields of from 39-60 percent (14,18).

A rather unusual synthesis of phenylboron dichloride was very briefly described in a note of Pace in 1929 (15). Benzene (40 g.) and boron trichloride (50 g.) were heated in a flask and the vapors passed through a tube containing platinized asbestos or a palladium black catalyst at 500°-600° C. A yield of 70 percent was claimed. It is difficult to see how such a high yield could be obtained since one would expect most of boron trichloride (B.P. 13° C) to distil over at first and the residual benzene (B.P. 90° C) would then boil and pass over the catalyst with insufficient boron trichloride for conversion to phenylboron dichloride.

In spite of doubts as to the yield claimed by Pace, it was decided to explore the catalytic method. It may be noted here that a DuPont patent (16) describes the preparation of β-chlorovinylboron dichloride from the vapor phase reaction of acetylene and boron trichloride over a mercurous chloride-granular carbon catalyst at 150-300° C. In the patent, the gases were metered into the reaction tube in the molar ratio of 1.5 to 1 with boron trichloride in excess in order to decrease the formation of bis-chlorovinylboron monochloride and tris-chlorovinylborine. The catalytic method, if practical, not only gives us a route to phenylboron dichloride but also to other dichlorides and their derived boronic acids starting with an unsaturated hydrocarbon. The avoidance of the Grignard step in the synthesis of boron derivatives

would lead to ease in scaling up the preparation of desired intermediates.

With these factors in mind we decided to design an apparatus for the catalytic vapor phase conversion of unsaturated hydrocarbons to substituted alkyl and aryl boron halides. The apparatus described in the experimental section (Fig. 2) was specifically suited to the preparation of phenylboron dichloride. Boron trichloride, in large excess, and benzene were passed through the catalyst tube and the excess boron trichloride condensed and recirculated in the system. A condenser or stripping column served to remove excess benzene and maintain a large molar excess to boron trichloride in the circulating vapor stream. The early runs gave little or no conversion to the desired product. The catalyst used in the early runs was a 2 percent palladium on granular charcoal of unknown composition and origin. In the early runs two additional factors tended to decrease the yield. The most serious factor was insufficient preliminary baking out of the catalyst to remove traces of water which reacted with BCl_3 to form a coating of boric acid and anhydride on the catalyst surface. Another factor may have been traces of sulfur in the regular solvent grade benzene. Beginning with the fifth run a reagent grade sulfur-free benzene was employed. Because of carbonization and etching of the glass in the early runs at about 500° C the bulk of the runs were held at that temperature. Later it appeared that the higher range of 550-600° C gave more rapid conversions, better yields, and did not appear to affect the catalyst adversely. In the last runs the catalyst appeared to be active for four days of operation before failing markedly. Since the main objective was the preparation of phenylboron dichloride further studies on the effect of variations in the catalyst were not carried out.

A total of 75.8 grams of pure phenylboron dichloride was obtained mainly from the last seven runs. Correcting for the removal of analytical samples the total product would have been 108 grams. Thus the daily yield per 6 hour run over a 125 ml. catalyst bed averaged about 14 grams per day. With continuous operation for 12 hours and a 625 ml. catalyst bed the daily output should be about 140 grams. This amount of material would be difficult to obtain in the laboratory by other methods unless pilot-

plant (12-22 liter flasks) Grignard facilities and an explosion proofed laboratory were available.

As mentioned earlier in the Introduction, a secondary portion of our work was directed toward the synthesis of Υ-dimethylaminopropaneboronic acid (Formula I) as an example of a "scorpion" type boronic acid.

The synthesis of the "scorpion" quadricovalent boronic acid was investigated following the work of Marxer (20,21) which describes the application of the Barbier type of concurrent Grignard reaction to dialkyl-aminoalkyl halides and metals in the presence of ketones. The metals specifically described are magnesium and potassium. In the experimental section attempts to utilize the reaction with dimethylaminopropyl chloride and methyl borate are described and discussed.

We obtained indications of low yields of the order of 5-10 percent of an amphoteric product corresponding in its properties to the expected dimethylaminopropane-boronic acid. This estimate was based on titration curves of the fractionated product as compared to those of boric acid and trimethylamine borate when titrated with alkali, both with and without, the addition of mannitol. This method of estimation was obviously un-satisfactory and our efforts were directed toward the actual isolation and characterization of the quadri-covalent "scorpion" boronic acid. Since the usual methods of separation of the reaction products by solvent extraction and crystallization were not successful chroma-tography, partition chromatography over silica gel and ion exchange techniques were attempted. No crystalline material corresponding to the desired acid was isolated. It became apparent that a semi-quantitative assay for the nitrogen content of each fraction would greatly facilitate the isolation of the acid. Due to the very large number of fractions obtained, the usual quantitative Dumas or Kjeldahl nitrogen analyses would be both time consuming and expensive. The sodium fusion methods of nitrogen detection are notoriously unreliable.

The first method studied for the detection of aminoboronic acids was the qualitative spot test for primary, secondary and tertiary amines described by

Feigl (22) using fused potassium thiocyanate. The complex and not fully understood reaction of the salt with amines at 200-250° C. gives hydrogen sulfide as one of the end products. In our hands the results obtained were frequently ambiguous. Very poor blanks were observed when lead acetate paper was used to detect the hydrogen sulfide as described by Feigl. The thiocyanate reaction did not seem worth while further investigating.

Our attention was called to a recent article on "A Method for the Detection of N-Dimethylamino Acids on Paper " which depended on the conversion of dimethylaminoacids to betaines by exposure of the paper grams (or spots on paper) to gaseous methyl iodide (23).

$$(CH_3)_2 \, N \cdot CHR \cdot COOH + CH_3I \longrightarrow$$

$$(CH_3)_3 \, \overset{+}{N} \cdot CHR \cdot COO^- + H^+ + I^-$$
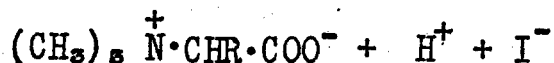
The liberated iodide ion was detected either by (a) oxidation with gaseous chlorine yielding iodine which gave a blue color on spraying the paper with starch solution or (b) precipitation of iodide as silver iodide followed by reduction with a photographic developer. The first method was developed earlier by /Rydon and Smith (5) but the second method was preferred by Kiessling and Porath and therefore first tried in our work.

We found that the presence of chloride ion in our fractions completely masked the iodide precipitation and subsequent development of the dark spot of reduced silver. We then developed a modified method based on the differential solubility of silver chloride and iodide in dilute aqueous ammonium hydroxide. After treatment of the paper with dilute silver nitrate to precipitate the combined halides the paper strips were suspended in clamps and washed with a flowing film of distilled water until all free silver ion had been removed. The strips were then treated with a flowing film of dilute ammonium hydroxide which differentially removed silver chloride leaving silver iodide. The paper was then treated with developer giving a black spot of silver where silver iodide was present. Although theoretically sound, the method was cumbersome and not as reliable as we had hoped.

It was then decided to investigate the chlorine-starch method of detection of iodide described by Rydon and Smith (24).

Erratic results were obtained in evaluating this method. It became apparent that the difficulties could be separated into two categories, first those dealing with the conditions of methylation with methyl iodide vapor, and second, the actual detection of iodide inn formed in the methylation process. Unfortunately the two stages were not independent since changes in concentration and pH of the buffer salts used in the process affected both steps. Much of the early work on varying conditions was nullified by the discovery that the chlorine oxidation step was extremely sensitive to the exact humidity of the papergram. A chance observation in one of the control series of steps seemed to indicate that the trace of moisture adsorbed by the paper from handling with the thumb was responsible for the lack of development of color in one case. This was confirmed and suitable drying and handling techniques developed. The work was, however, abandoned due to our inability to obtain consistent results in the presence of an excess of salts.

Since the completion of this work we noted an article in Nature (25) which also deals with the detection of iodine-containing compounds on paper chromatograms. The authors employ the ceric sulfate-arsenious acid method also used by Bowden et al (26). Because the work since 1 June has concentrated on the borazole phase of the project, the ceric sulfate-arsenious acid method has not been experimentally investigated.

A number of Marxer reaction runs were made but due to inadequate separation methods no γ-dimethylamino-propaneboronic acid was isolated.

At present, work is in progress in the characterization of tri-B-phenylborazole from the reaction of phenylboron dichloride and gaseous ammonia. A quantitative yield of material melting at 184-5° can be obtained. The infrared and molecular weight determinations agree with the expected values for the tri-B-phenylborazole but the analyses are not too satisfactory. An indication of the very high thermal stability of the borazole is the

fact that combustion analyses for nitrogen by the Dumas method are several percent lower than those obtained by a peroxide Kjeldahl digestion which gives almost theoretical values.

Of interest in connection with this work is the preliminary report by C. A. Brown on the reaction of boron trichloride and phenylboron dichloride with aromatic phenylenediamines (33).

III. CONCLUSIONS

A new, simple, and efficient synthesis of boron substituted alkyl and aryl borazoles has been developed in which an alkyl or aryl boron dichloride is reacted with ammonia. The yield under suitable conditions can be quantitative. The borazoles which have unusual thermal stability and in certain cases unexpected hydrolytic stability will be evaluated as lubricants and hydraulic fluids. The basic synthesis can be exploited in the preparation of boron containing polymers.

The primary bottle-neck in the synthesis of substituted borazoles is in the preparation of the alkyl and aryl dihalide intermediates. Considerable progress has been made by the successful development of a catalytic method of synthesizing phenylboron dichloride from benzene and boron trichloride.

IV. PLANS AND RECOMMENDATIONS

The preparation of a representative series of borazoles by our new synthesis from alkyl and aryl boron dihalides is being undertaken. Sufficient material will be prepared for evaluating these derivatives as lubricants and hydraulic fluids as well as laying the groundwork for an extension of the semi-inorganic polymer project outlined in earlier reports.

The new synthesis of borazoles will be extended by the use of other alkyl and aryl boron dihalides. In addition to ammonia, the use of monoalkylamines will be explored to give boron and nitrogen substituted borazoles. The unexpected stability of these alkylated borazoles and the simplicity of the new synthesis make the program very attractive in the production of a great many types of substituted borazoles. Of interest in the semi-inorganic polymer field is the use in this synthesis of diamines such as ethylenediamine or unsymmetrical dialkylaminoethylenediamines, aromatic diamines, and heterocyclic diamines in which one of the amino groups acts solely as a donor to complete the octet of the boron atom. It is expected that the synthesis with diamines may lead to linear polymers instead of borazoles, thus,

$$R-BCl_2 + NH_2-(X)_n- NR_2'$$
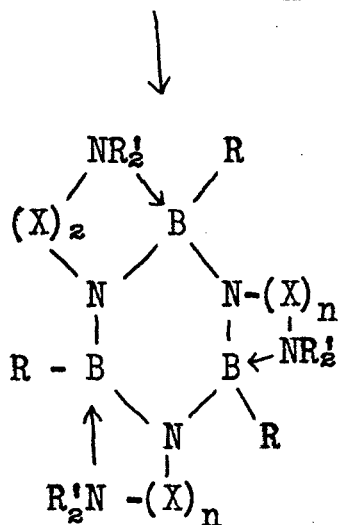
V
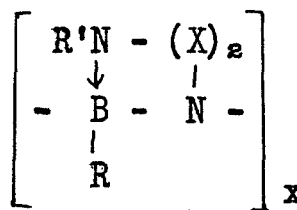
VI

where R = alkyl or aryl or H

R' = alkyl (methyl) or H

x = Linear or cyclic carbon chain

n = 2, 3, or 4

The simplest example of a linear polymer follows,

$$\left[\begin{array}{ccc} H_2N-CH_2-CH_2 \\ \downarrow \qquad \uparrow \\ -B-\!\!\!-\!\!\!-N- \\ | \\ CH_3 \end{array} \right]_x$$
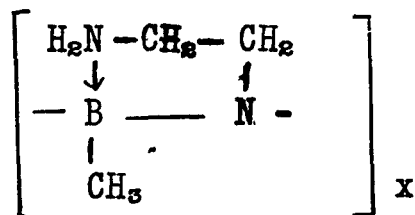
VII

This program of polymer synthesis as applied to linear polymers was presented first by the present investigator at the Air Force Contractors' Meeting in September 1954 and the formation of borazole reported at the May 1955 meeting. Also of interest at the present time are trifunctional borazoles derived from this synthesis which could serve as monomers for polymers and plastics of the amino-triazine or polyester type, -

$$\begin{array}{c} R \\ | \\ B \\ \diagup \quad \diagdown \\ NH_2 \cdot CH_2 \cdot CH_2 \cdot N \qquad N \cdot CH_2 \cdot CH_2 \cdot NH_2 \\ | \qquad\qquad | \\ RB \qquad\quad BR \\ \diagdown \qquad \diagup \\ N \\ | \\ CH_2 \cdot CH_2 \cdot NH_2 \end{array}$$

VIII

and

$$
\begin{array}{c}
\text{R} \\
| \\
\text{B} \\
\diagup \quad \diagdown \\
\text{HO·CH}_2\text{·CH}_2\text{·N} \qquad \text{N·CH}_2\text{·CH}_2\text{·OH} \\
| \qquad\qquad\qquad | \\
\text{RB} \qquad\qquad\quad \text{BR} \\
\diagdown \quad \diagup \\
\text{N} \\
| \\
\text{CH}_2\text{·CH}_2\text{·OH}
\end{array}
$$
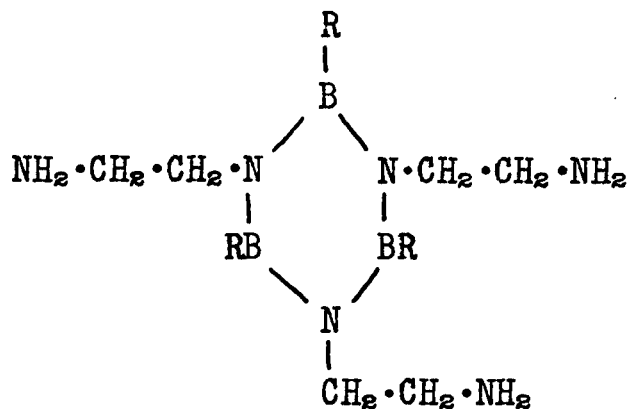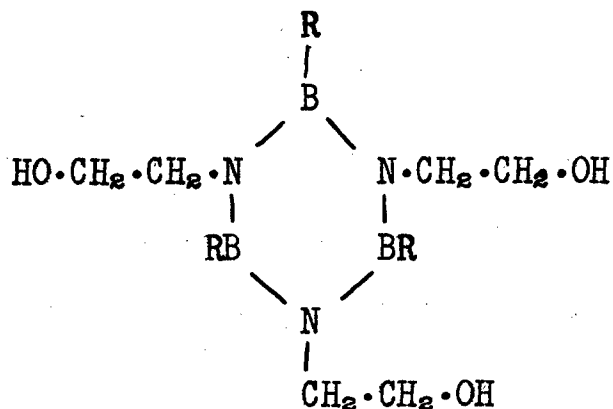
IX

Both these monomers (VIII and IX) when incorporated
into polymers might show considerable stabilization
through dative bond formation of the nitrogen or
oxygen atoms of the chain. From steric considerations
the monomer derived from ethylenediamine seems most
likely to show this effect (Formula VIII).

The major experimental program in progress will
still be, for some time, the development preparative
methods for the alkyl and arylboron dihalide intermediates.

V. EXPERIMENTAL

1. The Synthesis of B-Tri-n-butylborazole.

The experimental procedure of Booth and Kraus (3) for the preparation of "n-butylboronimine" was followed as closely as possible except for the extraction with benzene. A three-neck 250 ml. flask equipped with a tru-bore stirrer, gas inlet, and mercury-trapped gas outlet was flushed with dry nitrogen and cooled to -80° in a dry-ice-acetone bath. Butylboron dichloride (5.4 g.) was transferred under nitrogen to the precooled flask under nitrogen. Dry ammonia gas was then condensed in the flask until about 100 ml. of liquid ammonia had collected. It was noticed that the initial addition of ammonia caused the appearance, first of white fumes and then the deposition of a white solid on the surface of the flask. Two grams of sodium was cut into small pieces under mineral oil, washed with pentane and flushed with nitrogen in a special solids addition flask (27). The sodium was added slowly with stirring while the dry-ice bath was removed and the ammonia slowly evaporated. Fresh ammonia (100 ml. of liquid) was condensed in the reaction vessel and slowly evaporated over a two hour period. The white solid on the upper portion of the flask was tested and found to be ammonium chloride. After the additional ammonia had evaporated, a pasty white solid remained. Nitrogen saturated with water vapor was then passed through the flask for one hour to destroy the sodium. Then 20 ml. of water was slowly added to the flask and finally 20 ml. of benzene. The layers were separated and the lower layer extracted with three additional portions of benzene. The benzene layer was dried, evaporated and distilled in a molecular still at seven microns at a pot temperature of 34°. There remained 95 mg. of a yellowish white powder in the still pot which did not melt below 250° C. The distillate (0.97 grams) was a clear colorless oil. Because the product distilled at 34° at 7 microns instead of at 100°C at 5 microns as reported by Booth and Kraus it was suspected to be tri-B-n-butylborazole. As such, the calculated yield was 29.6%.

2. Identification of "n-Butylboronimine" as B-tri-n-Butylborazole by Boiling Point Calculations.

The boiling point of the product was 34° at 5 microns. The molecular weight of B-tri-n-butylborazole is 248.84. The corresponding benzenoid hydrocarbon, tri-n-butylbenzene, $C_{18}H_{30}$, is 246.42. The $C_{18}H_{30}$ hydrocarbons hexaethylbenzene and tri-t-butylbenzene boil at from 296-305° C. at 760 mm. as given in Beilstein. Taking 300° C. as the boiling point and using a vapor pressure-temperature Nomograph (Nomo Charts Co., P.O. Box 111, Roselle, NJ) the boiling point at 100 mm. was 148° C. and at 1 mm. was 100° C. When these values were plotted on 3 cycle semi-log paper with log p plotted against the reciprocal of the absolute temperature the extrapolated boiling point at 10 microns was 33° C. and at 5 microns was 24° C. Our observed boiling point of 34° at 7 microns thus corresponds to that of a benzenoid hydrocarbon of comparable molecular weight. As a matter of interest the b.p. of 105° C. at 5 microns observed by Booth and Kraus was in a reverse manner extrapolated and the boiling point at 760 mm. estimated to be 470° C. From the tables of the "Selected Values of the Properties of Hydrocarbons" (28) the boiling of n-triacontylbenzene, $C_{36}H_{66}$. M. W. 498.9, was found to be 496° at 760 mm. The molecular weight of the "butylimine" polymer as deduced from this comparison and the higher boiling point reported by Booth and Kraus would be slightly less than the hexamer.

3. B-tri-n-Butylborazole

(a) Chemical and Physical Properties

Booth and Kraus reported their "butylimine" to be extraordinarily resistant to decomposition by alkaline peroxide. We found the material to be apparently unaffected by H_2O, 6 N NaOH and 50% KOH. With 6N HCl a precipitate formed at the interface after standing 1 hour and with concentrated H_2SO_4 a solid immediately formed which slowly dissolved on standing.

The refractive index was determined on a redistilled sample and found to be $[N]_D^{25.5} = 1.4482$.

(b) Molecular Weight Determination

A molecular weight determination was done by measuring the freezing point depression in p-xylene. A sample of 0.111 grams in 15 ml. p-xylene (density 0.86) gave a depression of 0.143°. Using Biltz's constant of 43.0 for p-xylene

$$\frac{M.W. \times 0.143 \times 15 \times 0.86}{100 \times 0.111} = 43.0$$

M.W. = 258.7 (Theory for $C_{12}H_{30}N_3B_3$ is 248.84)

Instead of Biltz's value, the freezing point constant of p-xylene was determined directly. A sample of 0.152 g. of anthracene depressed the melting point of 15 ml. of p-xylene by 0.272° C.

$$K = \frac{178.22 \times 0.272 \times 15 \times 0.86}{100 \times 0.152}$$

$$K = 41.34$$

Using this directly determined value of K, the molecular weight of the unknown was recalculated and found to be 248.74. This close agreement with the theoretical value of 248.84 is fortuitous since the observed individual melting point readings varied by as much as 0.005° C.

(c) Analyses

A sample of 0.1230 grams of the borazole was dissolved in 5 ml. concentrated H_2SO_4, heated on the steam bath and cooled. About 1 ml. of 30% hydrogen peroxide was added dropwise with heating until the solution was colorless. The solution was cooled and an excess of 6 N sodium hydroxide was carefully added to the acid solution in a Kjeldahl type apparatus. The ammonia was distilled off, collected in standard N/10 HCl solution and back titrated with N/10 sodium hydroxide. The ammonia was equivalent to 14.80 ml. The basic residue from the Kjeldahl distillation was adjusted to the methyl-red end-point with HCl, heated to remove

CO_2, mannitol added and titrated to the phenolphthalein end point with 14.19 ml. of N/10 NaOH.

Anal. Calcd. for $C_{12}H_{30}N_3B_3$: N, 16.89; B, 13.04

Found: N, 16.83; B, 12.49 (See following

for additional boron value)

The borazole was redistilled rapidly at 45° and 6 microns and the boron analysis repeated using a 0.1007 gram sample. In this analysis the sulfuric acid-H_2O_2 solution was heated and refluxed (without allowing the escape of vapor from the test-tube). To the basic solution was added 1.5 ml. of 30 percent peroxide and the mixture refluxed to remove ammonia. The mannitol titration required 11.83 ml. of N/10 NaOH.

Anal. Calcd. for $C_{12}H_{30}N_3B_3$: B, 13.04,

Found: B, 12.71%

(d) Infrared Spectrum

The infrared spectrum of a thin film of liquid B-tri-n-butylborazole was recorded with a Perkin-Elmer 21-B double beam spectrophotometer.

The following table gives the observed results together with the corresponding reported absorption bands for borazole and the tentative assignments.

TABLE I

Infrared Spectra of Borazoles

Absorption, cm⁻¹		Assignments[1]
B-tri-n-butylborazole (Experimental Values)	Borazole (Literature Values)	
712	717	aromatic ring resonance
-	756	ring rocking
(775)	778	-
(797)	790	-
893	917	-
1090	1098	NH bending
1351 S	-	B-C absorption

Table I (Continued)

Absorption, cm^{-1} B-tri-n-butylborazole (Experimental Values)		Borazole (Literature Values)	Assignments [1]
(1408)		-	-
1475		1465	-
2900	S	-	C-H stretching
3430		3450-90	N-H stretching

Starred values indicate over 50% absorption and are the strongest peaks; values for minor peaks are enclosed in parentheses.

S - Absorption due to side chain (not present in borazole itself). (1) The values for borazole and the assignments are taken from the literature (29,30). The boron-carbon assignment 1320-90 (doublet) was tentatively proposed by Rochow (31).

4. **Synthesis of B-tri-n-butylborazole from n-Butylboron Dichloride and Ammonia**

The reaction of n-butylboron dichloride and ammonia was carried out in a three-neck apparatus as described previously in section 1 on "n-butylboronimine". Under an atmosphere of nitrogen, about 100 ml. of liquid ammonia was condensed in a flask cooled to -80° C. and to which had previously been added 5.4 g. of n-butylboron dichloride. The dry-ice bath was removed and it was noted that the liquid ammonia overlay a solid material which dissolved as the ammonia warmed up and boiled off. During the vaporization of the ammonia white fumes appeared and a yellow oil separated at the bottom of the flask. Finally when the ammonia had evaporated completely a pasty semi-solid material remained in the flask. The mass was broken up, extracted with 50 ml. of benzene, filtered, and washed with an additional 25 ml. of benzene. The solvent was evaporated under nitrogen and gave 2.408 g. of a slightly cloudy yellowish oil. The yield of crude B-tri-n-butyl-borazole was thus 74.6%. The oil was distilled in a micro still at 40° C. and 11-12 microns yielding 2.04 grams of a clear, colorless, mobile liquid; $[N]_D^{25.5} = 1.4482$. A

boron analysis was done on a 0.1033 gram sample by digestion with sulfuric acid - 30% H_2O_2 followed by a mannitol titration; 12.62 ml. of N/10 NaOH were consumed.

Anal. Calcd. for $C_{12}H_{30}N_3B_3$: B, 13.04

Found: B, 13.22

5. Benzeneboronic Acid

Benzeneboronic acid is a potential intermediate for the preparation of the phenylboron dichloride needed for the synthesis of B-triphenylborazole. Further work is reported on its preparation by the Grignard reaction with methyl borate, supplementing section 30 of the last final report (2). In this report a detailed description of the method of procedure was given. This is now supplemented by the diagram, Fig. 1. In the earlier report two runs using this apparatus were tabulated. Four additional runs were made and these are now recorded in Table II.

TABLE II

Synthesis of Benzeneboronic Acid

Run (a)	Addition		Hydrolysis	Yield
	Time Hrs.	Temp.°C	Temp.°C	%
1 (a)	4	0	25	25.6
2 (b)	4	0	25	23.9
3	3	0	25	24.2
4	7	-80	-80	74.2
5	6	-80	-80	74.5
6	5	-80	-80	74.2
7	5	-80	-80	65.0
8	5	-80	-80	72.0
9	4-1/2	-80	+25 (c)	70.3

(a) Runs 1-3 were early runs in which the drip-tip to direct the Grignard reagent into the center of the stirred vortex of methyl borate was not used. This device (See Fig. 1) seems to us to account more than any other single factor for our high yields. Runs 4, 5, 6, 7, and 9 used 57.5 grams of methyl borate (or a 15% excess). The other
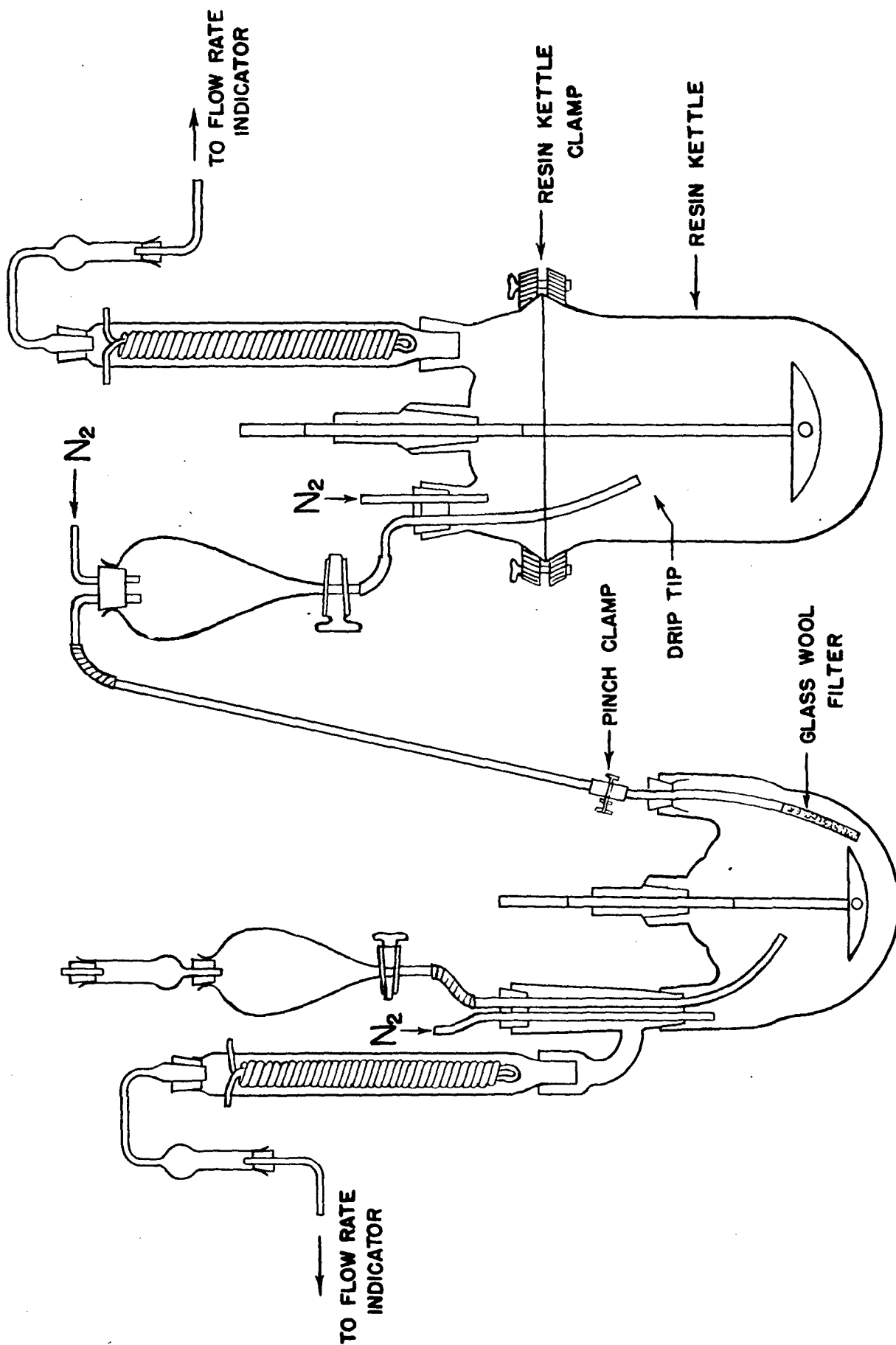
Fig. I GRIGNARD APPARATUS

runs used 50 grams or the theoretical amount. No apparent difference in yield (based on the amount of Grignard) was noted in using an excess of methyl borate.

(b) The purification method used in runs 1 and 2 was through the sodium salt-ether extraction method (17,18). Hutto's recent study gave a top yield of 38.8%. Bean and Johnson (17) reported yields of 50-60% with quarter-molar runs. On larger runs the yield rapidly dropped to 42-47%. Our own runs were 0.48 molar or about double those reported by Bean and Johnson.

The products obtained in runs 3-7 were purified by the carbon treatment method described earlier. Since this work was completed we read the recent publication of Torssell (14a) who obtained a maximum yield of 60% although the tolylboronic acid yields ranged from 47-51 percent. With the exception of run 7, our last five runs gave yields of over 70 percent. Torssell's method of purification using a pentane wash is superior to ours, however, and gives a cleaner product. We have followed his method of pentane washing to remove the diphenyl and the losses involved are less than 5 percent. Thus our preferred method of purification is to extract the crude, moist benzeneboronic acid with pentane and, after drying, recrystallizing from hot water after treatment with a small amount of carbon (5% by weight).

(c) In runs 4-8 the hydrolysis of the Grignard was carried out by slowly adding the dilute sulfuric acid to the ether suspension at -80° and then gradually thawing the suspension plus the frozen water. In run 9 the suspension was allowed to warm to room temperature (25° C) before adding the dilute acid. The acid was added to the constantly stirred ether suspension through the "drip-tip" and the hydrolysis mixture cooled with an external ice-bath to maintain the temperature at 25°C.

6. <u>Attempted Preparation of Phenylboron Dichloride by the Chlorination of Benzeneboronic Acid</u>

In December 1953, attempts were made to prepare phenylboron dichloride from benzeneboronic acid by replacing the hydroxyls with chlorine. The treatment of benzeneboronic

acid in benzene solution with phosphorus pentachloride
dehydrated the acid and gave the trimeric anhydride. No
phenylboron dichloride was isolated from this attempt.
On June 2, 1955 a private conversation with Professor
C. A. Brown of Western Reserve University, confirmed the
fact that the preparation of the dichloride is not a
simple procedure with the usual reagents employed in the
synthesis of acid chlorides. Professor Brown has con-
tinued work on the problem.

7. Catalytic Conversion of Benzene to Phenylboron Dichloride
   with Boron Trichloride

        Pace (15) in 1929 published a brief note on the pre-
paration of phenylboron dichloride by passing the vapors
of a mixture of boiling benzene and boron trichloride over
a palladium black or platinized asbestos catalyst at
500-600° C. The yield of 70 percent appears somewhat
optimistic in view of the relative vapor pressures of
benzene and BCl_3.

        We constructed the apparatus illustrated in Fig. 2
in order to recirculate benzene and boron trichloride
continuously through the catalyst tube. The boron
trichloride was present in large excess in the vapor
thus minimizing the formation of secondary products
such as diphenylboron monochloride and triphenylborine.

        The diagram is self-explanatory. The operation of
the apparatus varied from run to run. Due to losses of
benzene by freezing out on the dry-ice condenser etc.
the yields are relative. This disadvantage is being
remedied by the introduction of a second helix-packed
stripping column just below the joint of the dry-ice
condenser. It has taken ten runs to develop a reason-
ably stable operating procedure. The main stumbling
blocks overcome in order were:

        (a) Inactive carbon catalyst support for the
palladium; solved by the use of Carbide and Carbon's
"Columbia" Grade CXAL Activated Carbon (low copper,
low ash material).

        It may be noted here that the cost of
unsupported palladium black as a catalyst as advocated
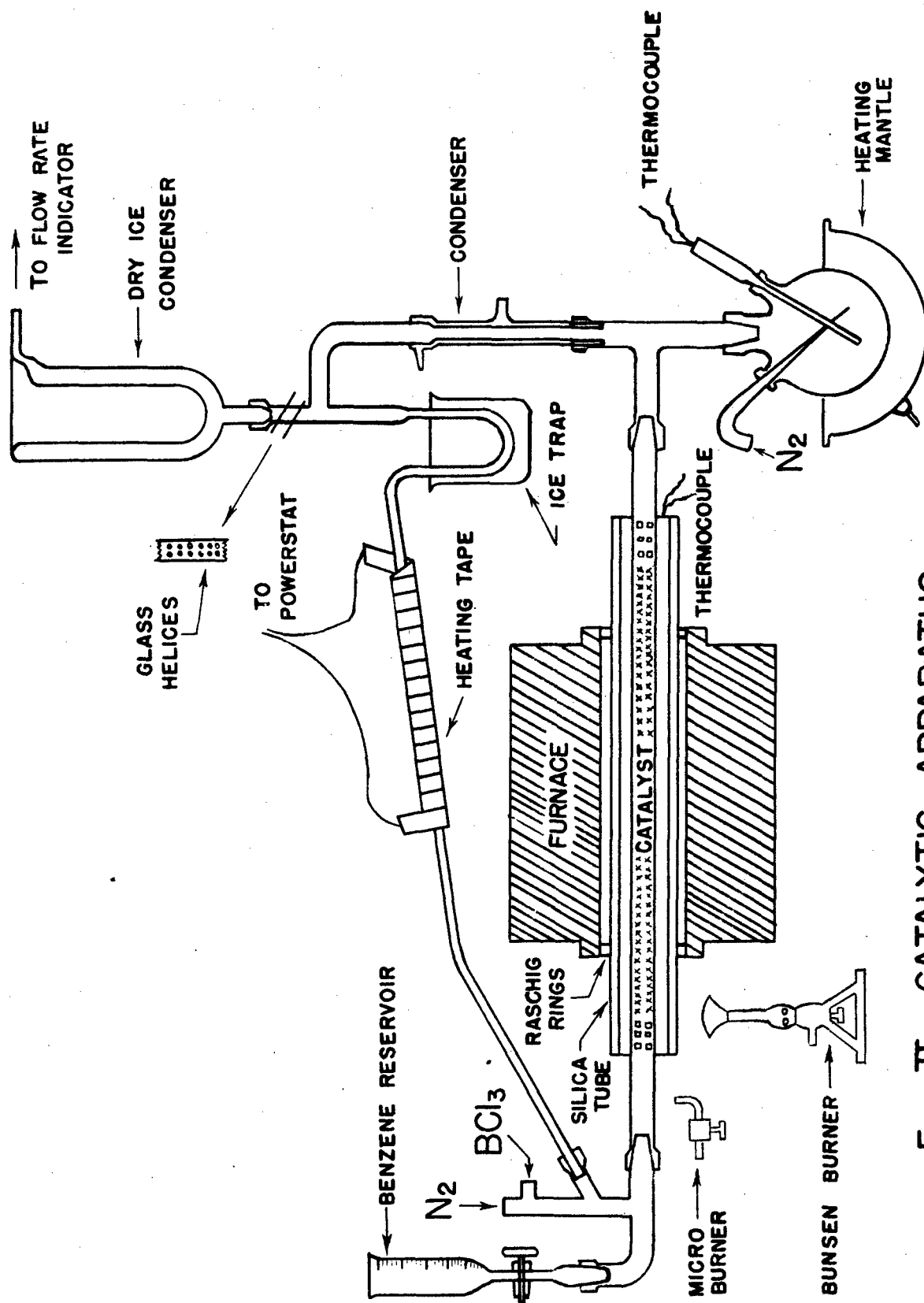by Pace would be prohibitive.

FIG. II CATALYTIC APPARATUS

(b) Sulfur in the benzene; solved by the use of a reagent grade benzene.

(c) Boric anhydride coating and consequent failure of catalyst; solved by prolonged (8 hour) baking out of the catalyst in situ at 500° C. and 1-2 mm. pressure. (Traces of moisture react with BCl_3 to give first boric acid and then the anhydride).

(d) Irregular operation and "slugging" over of excess BCl_3 from the trap. This "slugging" of the BCl_3-benzene mixture at times was uncontrollable in early runs and probably led to cooling of the catalyst by the large excess of vapors formed. This in turn led to inactivation of the catalyst and failure to convert the benzene which in a vicious cycle continued to pile up material in the U-trap and aggravate the "slugging." This condition was solved by replacing the glass wool (runs 1-9) plugs used to retain the catalyst by glass Raschig rings held in place by indentations in the catalyst tube.

The results of the first 14 runs are given in Table III.

TABLE III

Catalytic Preparation of Phenylboron Dichloride

Run	Catalyst	T° C.	% $C_6H_5BCl_2$(h)	Grams $C_6H_5BCl_2$	
1	5% Pd-C (a)	400+	0	0	
2	2% Pd-C (b)	510	13.65	3.7	
3	2% Pd-C (b)	510	14.69	5.3	
4	2% Pd-C (b)	550	7.16	2.4	
5	2% Pd-CXAL (c)	530	34.8	7.9	
6	2% Pd-CXAL	500	44.0	12.2	
7	Hg_2Cl_2-CXAL	175	0	0	
8	10% Pd-CXAL	475	76.4	30.0	(e)
9	10% Pd-CXAL	525	0	0	(f)
10	10% Pd-CXAL (d)	530	44.0	8.3	
11	10% Pd-CXAL	530	80.0	10.5	
12	10% Pd-CXAL	530	40.5	11.4	
13	10% Pd-CXAL	600	50.9	10.9	
14	10% Pd-CXAL	600	43.0	5.7	(g)

(a) The carbon used was 40-150 mesh and plugged in operation almost immediately.

(b) 8-10 mesh carbon of unknown origin.

(c) Carbide and Carbon's Columbia 4/6 mesh Special Catalyst grade low ash low copper activated carbon used for all runs subsequent to and including run 5.

(d) Runs 10-14 (4 runs) were made without changing the catalyst.

(e) Run 8 was a 3 day run with practically no material formed on the third day.

(f) Attempted regeneration of catalyst with methyl alcohol failed to give any product. This regenerative procedure will be repeated.

(g) In run 8 it was noted that conversion seemed to increase at temperatures around 530° over that at 500°. Runs 10-14 were made on the same catalyst in situ (without change). Previously, after about 12 hours operation (see Run 8) the catalyst failed. The decrease in yield in run 14 on the fifth day may be due to the higher temperature of 600° used the previous day for run 13.

(h) This column gives the percent of phenylboron dichloride in the pot sample as obtained by direct analysis. Multiplied by the total weight of material, the yield of phenylboron dichloride is obtained and is tabulated in the last column.

From the combined material of most of these runs (minus material withdrawn for analyses, etc.) a total of 75.8 g. of phenylboron dichloride b.p. 75°/30 mm. was obtained. The density of a 2 ml. sample was approximately 1 19.

This method of preparation of phenylboron dichloride appears practical and for larger amounts of material an increased catalyst volume would be recommended. The product of the reaction is a clear fuming liquid with some benzene and BCl_3 present, both of which may readily be removed by distillation. Only traces of biphenyl are formed as can be noted by the odor of hydrolyzed samples.

Since the operation is becoming rapidly stabilized on a production basis the description and further details will be reserved for a subsequent report.

8. Assay Method for Phenylboron Dichloride

Incidental to the development of the catalytic method of preparing phenylboron dichloride a method of assay was devised suitable for use in the presence of benzene, boric acid, boron trichloride and traces of diphenyl.

Procedure for Assay:

A two ml. sample (10-80% $C_6H_5BCl_2$) was pipetted into a tared weighing bottle and weighed. [In early runs of 0-10% material, 5 ml. samples were taken for each analysis.].

The sample was decomposed by pouring drop by drop onto 25 ml. of crushed ice in a 150 ml. beaker. The aqueous solution was made alkaline with 10 ml. of 12 N sodium hydroxide and extracted twice with 25 ml. portions of ether (discarded) to remove traces of diphenyl. The residual alkaline extract was acidified with 12 ml. concentrated hydrochloric acid and extracted with three 15 ml. portions of ether. The combined ether extracts were evaporated and the residue taken up in 25 ml. of hot water. The aqueous solution of benzeneboronic acid was transferred to a 125 ml. Erlenmeyer flask and 4 gms. of mannitol added for each 25 ml. of volume. The solution was then titrated with N/10 NaOH to the phenolphthalein end point.

1 ml. of N/10 NaOH = 0.1588 g. $C_6H_5BCl_2$

9. Preparation of Catalysts for Phenylborondichloride

A description of the preparation of the earlier catalysts will be omitted because of the poor yields obtained. The 2% palladium catalyst was prepared as follows

To 125 ml. (apparent density 0.445) of coconut charcoal of catalyst grade in pellet form, and low in copper and ash [Carbide and Carbon's "Columbian" Activated Carbon CXAL, 4-6 Mesh], was added a solution of palladium

chloride in 60 ml. H₂O containing a minimum amount of free hydrochloric acid. The palladium chloride solution was prepared by dissolving 1.79 g. of palladium chloride in a minimum amount of conc. hydrochloric acid in a porcelain casserole and evaporating cautiously over a steam bath with the aid of a nitrogen stream until only a slightly moist residue remained. To this moist residue was added 60 ml. of water. The palladium chloride solution decolorized in a few minutes when poured over the carbon and rapidly stirred. No other reducing agent was used. The catalyst was washed thoroughly and then dried under nitrogen and in vacuo in the catalyst tube at 500° C.

The same procedure did not work with the 10% palladium catalyst and formaldehyde was used as a reducing agent. To 20 grams of palladium chloride (60.1% Pd = 12 g. palladium) in a casserole were added several portions of conc. HCl and the solution evaporated on the steam bath to apparent dryness. An excess of 15 ml. conc. hydrochloric acid was added and, after solution of the chloride, diluted with 110 ml. of water. The solution was poured over 108 grams of CXAL carbon and stirred. The supernatent liquid was brownish yellow. The suspension was made alkaline with sodium hydroxide while being stirred and warmed over a steam bath. To the hot solution was added 15 ml. of 40% formalin and the mixture stirred. The catalyst was washed thoroughly with water and dried in the catalyst tube as before. When a large batch of catalyst was made up at one time, the bulk of the material was kept moist with water and only each 125 ml. portion dried by baking out separately in the catalyst tube.

A mercurous chloride catalyst was also prepared using CXAL carbon. This was prepared by reducing a solution of mercuric chloride with sulfur dioxide essentially according to the procedure described in a DuPont patent by H. R. Arnold (16). This catalyst was used in run 7 (Table II) but no product could be isolated.

10. Preparation of Tri-n-butylborine

For the preparation of tri-n-butyl-B-borazole and its N-substituted derivatives large amounts of n-butylboron dichloride were required. For the latter material, the intermediate is tri-n-butylborine.

The preparation of tri-n-butylborine was carried out by the normal Grignard reaction with a boron halide essentially as described by Johnson et al (17) who states yields of 80% falling to 50% when methyl borate is substituted for the boron trifluoride. Johnson's choice of boron trifluoride as the halide depended upon its availability (1938), cost, and ease of handling and purification of the etherate. In some cases we used the boron trifluoride etherate but found that the glassware was badly etched after the Grignard hydrolysis with acids during which some HF is liberated. In all but the first run, butyl chloride rather than the bromide was used to prepare the Grignard reagent.

The apparatus used was similar to the resin kettle set-up illustrated in Figure 1. Since the synthesis required the addition of the halide to the Grignard reagent (Normal Grignard) the procedure differed from the benzeneboronic acid preparation. The Grignard reagent formed in the round-bottom flask was pumped over into the resin kettle instead of the separatory funnel. The reason for this double operation is the use of a large excess of magnesium in the preparation of the reagent which is filtered during the pumping operation. Also in the borine synthesis, an additional siphon tube was inserted whose end extended to the bottom of the resin flask. This was used to force out, under nitrogen pressure, the aqueous layer and wash liquors after the Grignard hydrolysis step.

Table IV gives the results of a series of runs. A combination of factors including the spontaneous inflammability and rapid oxidation of the borine coupled with the small size of the only suitable available column packed with 3 mm. glass helices 1 X 55 cm.) for vacuum distillations limited the operations. Including down time, each distillation took a minimum of four days.

TABLE IV

Preparation of Tri-n-butylborine[a]

Run	Halide	Moles	Yield Percent Crude	Pure	Pure Product [d] Grams
1 (b)	BCl_3	0.425	39%	(c)	(c)
2	BF_3	0.425	47.5%		
3	BF_3	0.425	56.4%		
4	BF_3	0.425	60.7	35.5	110.0
5	BCl_3	1.0)		72.6%	264.6
6	BCl_3	1.0)			

(a) For runs 1-4 0.425 moles of halide and 1.47 moles
    (15% excess) of Grignard reagent were used. In
    runs 5 and 6, 1.0 mole halide and 3.01 moles
    Grignard were used. The amounts of ether used
    in runs 5 and 6 were Grignard, 1400 ml.; BCl_3
    solution, 800 ml.; and additional at end of run
    to thin out pasty suspension, 500. total, 2700 ml.
    For hydrolysis 300 ml. of conc. HCl and 400 ml.
    of water were used.

(b) In run 1, butyl bromide was used to form the
    Grignard reagent. In subsequent runs, butyl
    chloride was used.

(c) The crude product of runs 1-4 inclusive were
    combined and fractionated to give the pure
    product.

(d) Analyses on the two pure fractions follow.

> Anal. Calc'd. for $C_{12}H_{27}B$: B, 5.94
>
> Found: B, (a) 6.36, (b) 6.07

The preparation of the borine gave difficulties due
to the inability of the stirrer to handle the heavy ether
suspension formed just prior to hydrolysis. A larger
(5 l.) resin kettle has been obtained for succeeding runs
so that additional ether can be added to thin suspension.

11. Preparation of n-Butylboron Dichloride

In our final WADC Technical Report 55-26 Part II, we
described the preparation of butylboron dichloride from
the borin and boron trichloride in the presence of aluminum
chloride. The yield of crude was 35.4% but only 10% of
pure material was recovered. This low yield was ascribed
mainly to manipulative losses. The dichloride is spontaneously
inflammable and extraordinarily sensitive to oxidation.

Recently the preparation was repeated on 42.4 grams
of pure analysed tri-n-butyl borine from free appreciable
amounts of oxides. The yield of pure butylboron di-
chloride was 8.05 grams or 8.3% in spite of improved
procedures which kept manipulative losses to a minimum.

It appears that when 5% AlCl$_3$ catalyst is used only
BCl$_3$ is recovered. The product was finally obtained using
40% by weight of "catalyst." The role of disproportionation
in the formation of the material and the possible re-
distribution during distillation has not been solved.
Active work is being continued on the problem. We are also
in the process of repeating the original work of Booth
and Kraus who prepared the halides by treating the borine
with hydrogen chloride both with and without the presence
of aluminum chloride as a catalyst.

12. Attempted Synthesis of γ-Dimethylaminopropaneboronic Acid

The first use of halogen-alkylamines in Grignard
reactions was described by Marxer in 1941 (20). In a later
patent (21) by Miescher and Marxer, the use of the alkali
metals is also disclosed. The intermediate chosen for
our initial work was γ-dimethylaminopropylchloride pre-
pared from the reaction of 1-chloro-3-bromopropane and
dimethylamine. A yield of 77.1 grams or 63.5% of material
boiling at 28-29° C. at 13 mm. was obtained. Marxer gave
a boiling range of 29-32° C. at 12 mm. for the product.
In another run a 68.4% of material, b.p. 28-30°/12 mm.,
was obtained. The material quaternized readily on warming
and was therefore stored in the freezer at -15° C. (It
was subsequently noted that γ-dimethylaminopropyl
chloride hydrochloride was available from the Michigan
Chemical Corporation).

(a) Grignard Reactions

As indicated by Miescher and Marxer the Grignard
product of the dialkylaminopropyl chloride is a solid.
Preliminary experiments confirmed this observation. When
dimethylaminopropyl chloride in ether solution was added
to a stirred suspension of magnesium in ether the turnings
become covered with a white layer of solid dimethylamino-
propyl magnesium chloride and very little reaction took
place. Various attempts at using Grignard starters, rapid
stirring, using a large excess of magnesium, and priming
with preformed ethyl magnesium bromide failed to increase
perceptibly the amount of Grignard reagent formed. The
examples given by Marxer were invariably simultaneous
reactions in which the alkyl halide and a ketone were added
concurrently to the magnesium metal suspended in ether.

Since we were unable to get any reaction by this pro-
cedure, a run was made in which ethylbromide in an
equimolar amount to the dimethylaminopropyl chloride
(10 grams or 0.082 moles) was used as a "continuous
activator" or "entraining" agent. Only partial reaction
of the magnesium (4 grams) occurred and a considerable
amount of white solid was formed. A sample of this solid
reacted violently with water. To the reactants cooled
to -80° was added, with rapid stirring, 20 grams of methyl
borate in 150 ml. of ether and the mixture stirred for
9 hours at -80°. The product was decomposed with saturated
ammonium chloride solution. A complicated fractionation
of the products was carried out based mainly on partition
of the components between ether and acid and alkaline
solutions. The only crystalline product isolated was
ethaneboronic acid, m.p. 92° (Koffler block).

Anal. Calcd. for $C_2H_7O_2B$; B, 14.64

Found: B, 15.00

The simultaneous Grignard reaction was repeated using
the same quantities of reactants as in the previous experi-
ment. In this run, also, the reaction of the magnesium
was far from complete. The methyl borate in ether was
added this time at room temperature instead of at -80°.
An exothermic reaction occurred with considerable refluxing
of the ether. After stirring overnight the mixture was
decomposed with 0.82 moles of sulfuric acid in 5% solution.

The separation procedure again was based on ether
partitions with aqueous solutions at various pH values.
Ethaneboronic acid was again isolated but no crystalline
material corresponding to the desired   Υ-dimethylamino-
propaneboronic acid.

(b) Potassium Reactions

Marxer, in his publication and in his patent,
claims the use of alkali metals, in general, in addition
to magnesium and zinc for the simultaneous reaction of a
dialkylaminoalkyl halide with a ketone. With the exception
of one illustrative reaction using potassium, all other
examples were with magnesium as the metal.

13. Attempted Determination of Dimethylaminopropaneboronic Acid in Chromatographic Fractions

Attempts were made to adapt the two methods of Kiessling and Porath (23) to the determination of dimethyl-aminopropaneboronic acid.

(a) Silver Nitrate Method

The presence of chlorides in the reaction product interferred seriously with the method. For the determination, a drop of the reaction product was spotted on paper. Control strips were spotted with 0.1 N KI admixed with an excess of 0.1 N NaCl. The dried paper was immersed in 0.1 N ammoniacal silver nitrate and then washed with a flowing film of 1% aqueous ammonium hydroxide for 15 minutes. The strips were then washed with a flowing film of water and developed in Eastman Kodak X-ray developer. The KI spot could be differentiated by this procedure. No extensive work was done further to test the sensitivity of the method. Results with the Marxer reaction products were positive but unfortunately some of the blanks were also positive and the method was abandoned.

(b) Chlorine Oxidation Method

Kiessling and Porath's second method of detecting the iodide ion formed in the methylation of dialkylamines with methyl iodide was by oxidation with chlorine, aeration of excess chlorine and spraying with starch solution to develop a blue color. This chlorine oxidation step was also described by Rydon and Smith (24) in connection with the detection of traces of iodide on papergrams.

Initial work was concentrated on the methylation step. Kiessling and Porath used paper which had been treated with 0.02 M sodium tetraborate solution as a buffer and dried. We obtained irregular results using triethanolamine as the amine and a series of buffered papers using bicarbonate, boric acid-borate and phosphate buffers. Both the concentration of buffer and pH of the papers were varied. It soon became apparent that the irregularity was not only in the methylation step but also in the chlorination and subsequent development of the blue spot on spraying with starch. The buffered papers were then treated with drops of varying concentrations of KI or

I in carbon tetrachloride. Eventually a drop of 0.002 N KI was used as the standard. Since the work was discontinued due to the pressure of the borazole program only the main conclusions will be abstracted.

(a) Traces of moisture (such as those caused by handling the paper with bare fingers) reduce very markedly the sensitivity of the color reaction. The paper was dried for at least 20 minutes at 110° C., handled with forceps and immediately dropped into a tall cylinder of dry chlorine over $CaCl_2$.

(b) The optimum period of chlorine treatment appeared to be 3 minutes. Longer periods resulted in loss of sensitivity.

(c) High concentrations of buffer salts seemed to be detrimental - particularly in the case of borate and bicarbonate buffers.

(d) The reaction appeared to be most sensitive near the neutral point. Best results (with KI, not with the methylation procedure) were obtained with unbuffered paper.

(e) When 1% KI was added to the 1% starch solution used for the final spray the sensitivity was markedly increased in some cases but this also led to a general blue background if all traces of chlorine were not removed.

14. Additional Marxer Reactions

The Marxer reaction was tried with Υ-dimethylaminopropyl chloride, methyl borate and either magnesium or potassium essentially as described earlier. Chromatographic and ion exchange methods of separating the amphoteric product were not successful due to our inability to estimate the total amphoteric acid in each fraction. In one run using potassium, the excess boric acid was volatilized as methyl borate by repeated evaporations with methanol but no amphoteric acid isolated. This method had not as yet been applied to reactions with magnesium.

15. Synthesis of B-Triphenylborazole

(a) Low Temperature-liquid Ammonia Method

When 28.3 grams of phenylboron dichloride was chilled to -80° in a 3 necked flask apparatus described in section V, 1 under the synthesis of B-tri-n-butylborazole, it solidified. A large excess of liquid ammonia was condensed in the flask while cooling with a dry-ice-acetone bath. The reaction mixture was allowed to gradually warm up and after the bulk of the ammonia had boiled off, 150 ml. of benzene was added with stirring. The suspension was filtered. The insoluble residue was mainly ammonium chloride. By evaporating the benzene solution a yield of 11.9 grams (64.9% of theory) of material m.p. 175° was obtained. The crude product was dissolved in benzene, treated with charcoal, filtered and the benzene filtrate washed twice with 0.1N NaOH and then twice with water and dried over anhydrous magnesium sulfate. On recrystallization from benzene-hexane or better, chloroform-hexane mixtures, the product formed needles m.p. 184-5°.

Anal. Calcd. for $C_{18}H_{18}N_3B_3$: C, 70.01;

H, 5.87; N, 13.61; B, 10.51.

Found: Sample 1, C, 72.81, 71.89; H, 6.66, 6.15;

N, 9.69, 9.85 (Dumas); 12.50, 12.64 (Kjedahl); B, 10.73.

Very serious difficulties with the analysis of organo-boron compounds and particularily borazoles have been noted previously in the literature (31, 34).

Preliminary molecular weight determinations by the freezing point method in p-xylene gave erratic and low results (N.W. 240). Using the Menzies-Wright ebullioscopic method with benzene as a solvent the molecular weight was found to be 335.6 and 323.1. Theory for triphenylborazole is 308.80.

(b) Room Temperature-Gaseous Ammonia Method

(Experimental work in part by Mr. Nathan G. Steinberg)
The yield of borazole was made almost quantitative by the following procedure. A solution of 5 cc. (5.95 g.) of phenylboron dichloride was dissolved in 50 ml. of dry benzene and placed in a three necked flask equipped with

stirrer and nitrogen inlet. Precautions were taken to maintain a nitrogen atmosphere and freedom from traces of water. The solution was stirred and cooled to 10-25° C. while a very slow stream of dry gaseous ammonia passed above the surface of the benzene for several hours until ammonia appeared in the flask exit nitrogen stream and the fog in the interior of the flask subsided. After stirring an additional hour the 50 ml. of benzene was added and the mixture heated with stirring to the boiling point. The solution was filtered hot from the ammonium chloride and concentrated to a small volume and an equal quantity of hot hexane added. on cooling the first crop of needles on drying weighed 3.57 g. m.p. 181-2. (92.7% of theory). The mother liquor gave an additional 0.27 g. m.p. 168-198°. The total yield was thus quantitative. The material on recrystallization from chloroform-hexane gave needles m.p. 184-5°. Analyses were not as yet any more consistent than those reported in section (a).

An infrared spectrum was run with a Perkin-Elmer Model 21 instrument in 1% chloroform solution. The following absorption peaks (cm^{-1}) were observed, (4050), 3450, 3010, (1950), (1890), (1820), (1680), 1605, 1450, 1335, (1290), (1250), 1200, (1060), (1030), (910), and 670.

These values are compatible with the values for borazole given in an earlier table (Section II).

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